REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE 26 January, 2001	3. REPORT TYPE AND DATES COVERED 1 July, 1999- 30 June, 2000 FINAL

4. TITLE AND SUBTITLE
The use of novel precursor chemistry for synthesis of superhard materials

5. FUNDING NUMBERS
DAAD19-99-1-0284

6. AUTHOR(S)
John Kouvetakis

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Arizona State University ,
Tempe, AZ 85287

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
U. S. Army Research Office
P.O. Box 12211
Research Triangle Park, NC 27709-2211

10. SPONSORING / MONITORING AGENCY REPORT NUMBER
ARO 40171.1 - MS - 11

11. SUPPLEMENTARY NOTES
The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The objective of this short term program was to initiate synthesis of a new class of light element materials with novel compositions that are isoelectronic to carbon (i.e. the number of valence electrons per atom is four) or related to Si_3N_4. The ultimate goal is to investigate their use in high pressure or laser ablation synthesis of extremely dense, superhard materials of the same composition that have structures and properties related to those of diamond. Examples of such systems include nitrogen rich compounds with stoichiometric compositions $BeCN_2$, $LiBC_2N_4$, $LiAlC_2N_4$, and C_3N_4. Progress on synthesis of the novel the phases $BeCN_2$, and $LiAlC_2N_4$, as well as initial high pressure studies of graphitic $C_3N_4 - LiBC_4N_4$ are described in this report. This work is continuing with full funding form ARO under grant DAA19-00-1-0471.

14. SUBJECT TERMS
solid state chemistry, hard materials, diamond-like solids, high pressure

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OR REPORT	18. SECURITY CLASSIFICATION ON THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev.2-89)
Prescribed by ANSI Std. 239-18
298-102

20010301 123

MASTER COPY: PLEASE KEEP THIS "MEMORANDUM OF TRANSMITTAL" BLANK FOR REPRODUCTION PURPOSES. WHEN REPORTS ARE GENERATED UNDER THE ARO SPONSORSHIP, FORWARD A COMPLETED COPY OF THIS FORM WITH EACH REPORT SHIPMENT TO THE ARO. THIS WILL ASSURE PROPER IDENTIFICATION. NOT TO BE USED FOR INTERIM PROGRESS REPORTS; SEE PAGE 2 FOR INTERIM PROGRESS REPORT INSTRUCTIONS.

MEMORANDUM OF TRANSMITTAL

U.S. Army Research Office
ATTN: AMSRL-RO-BI (TR)
P.O. Box 12211
Research Triangle Park, NC 27709-2211

January 26, 2001

☐ Reprint (Orig + 2 copies)

☐ Technical Report (Orig + 2 copies)

☐ Manuscript (1 copy)

X Final Progress Report (Orig + 2 copies)

☐ Related Materials, Abstracts, Theses (1 copy)

CONTRACT/GRANT NUMBER: DAAD19-99-1-0284

REPORT TITLE: The use of novel precursor chemistryfor synthesis of superhard materials

is forwarded for your information.

SUBMITTED FOR PUBLICATION TO (applicable only if report is manuscript):

Sincerely,

J Kouvetakis

JOHN KOUVETAKIS

Final Technical Report

Project Title
The use of novel precursor chemistry for synthesis of superhard materials,

Author
J. Kouvetakis

ARO Award Number
DAAD19-99-1-0284

Period Covered
7/1/99 - 6/30/2000

1. Statement of the Problem

The objective of this short term program was to initiate synthesis of a new class of light element materials with novel compositions that are isoelectronic to carbon (i.e. the number of valence electrons per atom is four) or related to Si_3N_4. The ultimate goal is to investigate their use in high pressure or laser ablation synthesis of extremely dense, superhard materials of the same composition that have structures and properties related to those of diamond. Examples of such systems include nitrogen rich compounds with stoichiometric compositions $BeCN_2$, $LiBC_2N_4$, $LiAlC_2N_4$, and C_3N_4. Progress on synthesis of the novel the phases $BeCN_2$, and $LiAlC_2N_4$, as well as initial high pressure studies of graphitic C_3N_4 – $LiBC_4N_4$ are described below.

2. Summary of the Most Important Results

$BeCN_2$

The unknown $BeCN_2$ phase is of particular interest because it has been predicted to have optical and mechanical properties that are superior to those of c-BN: i.e. it is a direct-bandgap semiconductor with a bulk modulus of 333 GPa. Three-dimensional $BeCN_2$ is structurally analogous to wurtzitic $BeSiN_2$ (a structure very similar to the chalcopyrite structure) and has a lattice constant nearly identical to that of cubic BN. We have adopted two strategies for preparation of $BeCN_2$ thin films and bulk materials: (a) synthesis, and decomposition of molecular $Be(NCN\text{-}SiMe_3)_2$ and (b) direct synthesis of bulk $BeCN_2$ by soft-chemistry methods.

The first method is intended to synthesize thin films of BCN_2 via decomposition of the volatile molecular source $Be(NCN\text{-}SiMe_3)_2$ by elimination of one equivalent of $Me_3Si\text{-}N{=}C{=}N\text{-}SiMe_3$ as illustrated by Eq 1 below.

$$Be[NCN\text{–}SiMe_3]_2 \rightarrow BeCN_2 + Me_3Si\text{-}N{=}C{=}N\text{-}SiMe_3 \quad (1)$$

We have recently succeeded in synthesis and identification of small quantities of $Me_3Si\text{-}N{=}C{=}N\text{-}SiMe_3$, however, larger yields of the molecule are necessary to pursue a systematic study of CVD growth of films and coatings. Development of an improved synthesis is currently underway. The second method utilized low temperature reactions of cyanamide (H_2CN_2) with $Be[N(SiMe_3)_2]_2$ to produce an intermediate solid precursor with composition $Be(NCNH)_2{\bullet}H_2CN_2$ (see Eq. 2) which was characterized by spectroscopic methods (IR, mass spectrometry) and elemental analysis. Annealing of this solid, at 750°C in vacuum produced a colorless pollycrystalline material and memamine (see Eq. 3) . Vibrational and combustion analysis data are consistent with "$BeCN_2$" although its structure still remains unsolved. The X-Ray powder pattern was virtually identical to earlier X-ray patterns of samples obtained from the reaction of equimolar amounts of $BeCl_2$ and TMS_2CN_2 (see Eq. 4).

$$Be[N(TMS)_2]_2 + 3H_2CN_2 \rightarrow \text{“}Be(NCNH)_2{\bullet}H_2CN_2\text{”} + 2HN(TMS)_2 \quad (2)$$

$$\text{“}Be(NCNH)_2{\bullet}H_2CN_2\text{”} \rightarrow \text{“}BeCN_2\text{”} + {}^2/_3\text{Melamine} \quad (3)$$

$$BeCl_2 + TMS_2CN_2 \rightarrow \text{“}BeCN_2\text{”} + 4TMS\text{–}Cl \quad (4)$$

The two different synthetic routes described by Equations 3 and 4 appear to yield the same product and our preliminary characterizations as well as the reaction intermediates clearly point to the desired $BeCN_2$ compound. A sturctural determination is, however, necessary to unambiguously identify this intriguing material. A possible polymeric structure of $BeCN_2$ is illustrated in Fig 1. The structure of $BeSiN_2$ analogous to dense $BeCN_2$ is also shown in Fig. 1.

Figure 1: Possible polymeric structure of Be(N=C=N). The structure of $BeSiN_2$ depicted as tetrahedra filled with Be (light) and Si (dark). Tetrahedra filled with the same atomsform zig-zag chains. The $BeCN_2$ compound is expected to have a similar dense structure.

$LiAlC_2N_4$

Initial attempts to prepare $LiAlC_2N_4$ involved reactions of $LiAlH_4$ as the Al and Li source, with $(SiMe_3)_2CN_2$ as the N-C-N source. As illustrated in the synthesis depicted by equation 5, complete elimination of gaseous $SiMe_3H$ affords the ternary compound $LiAlN_2CN_2$. However, it was discovered that the crystalline solid $Al(TMS\text{–}NCHN\text{–}TMS)_3$ is the main product derived from this method instead (see Eqs 6 and 7 below).

$$LiAlH_4 + 2(SiMe_3)_2CN_2 \rightarrow LiAl(CN_2)_2 + 4SiMe_3H \quad (5)$$

$$LiAlH_4 + TMS_2CN_2 \rightarrow LiNCN\text{–}TMS + \text{“}AlH_3\text{”} + Me_3SiH \quad (6)$$

$$\text{“}AlH_3\text{”} + 3TMS_2CN_2 \rightarrow Al(TMS\text{–}NCHN\text{–}TMS)_3 \quad (7)$$

Single-crystal X-ray diffraction revealed a novel structure for ($AlC_{21}H_{57}N_6Si_6$) in which one aluminum atom is coordinated by six nitrogen atoms as shown in Fig. 2. Although ($AlC_{21}H_{57}N_6Si_6$) was not the targeted product, its synthesis led to a new class of compounds incorporating the sterically crowded $(TMS\text{–}NCHN\text{–}TMS)^{-1}$ bidentate ligand. The analogous Ga compound $Ga(TMS\text{–}NCHN\text{–}TMS)_3$ as well as the related hydrides

$HGa(TMS–NCHN–TMS)_2$ and $H_2Ga(TMS–NCHN–TMS)$ were also synthesized as volatile molecular species. Preliminary experiments suggest that the corresponding Al hydrides are also possible. These results indicate that the most important application of this new reaction method is the preparation of stable and volatile Al and Ga hydrides of the general formula $RGaH_2$ and R_2GaH [where R= (TMS–NCHN–TMS)]. These may be potentially useful as CVD precursors for growth of group III nitrides and related optoelectronic III-V materials. We are currently attempting to utilize this method to prepare the indium analogs $RInH_2$ and R_2InH as well as related unimolecular InN sources such as $RInHN_3$. The large chelating group R is the key to stabilizing such compounds which are typically considered to be unstable.

Figure 2: Molecular structure of $Al(Me_3Si–N–C–N–SiMe_3)_3$

Further attempts to synthesize the desired $LiAl(NCN)_2$ and possibly $LiGa(NCN)_2$involve reactions of alternative lithium, Al and Ga sources such as $LiAlCl_4$ and $LiGaCl_4$. We found that the reaction of $LiAlCl_4$ with $Me_3Si\text{-}N{=}C{=}N\text{-}SiMe_3$ at 650 °C results in a pollycrystalline colorless material which displays lattice modes consistent with a three dimensional inorganic solid. The IR spectrum is very simple and shows a sharp peak at 2190 cm^{-1} corresponding to ν_{as} for the linear $N{=}C{=}N^{-2}$ moiety, and additional peaks at 536 cm^{-1} and 470 cm^{-1} which can be assigned to metal-carbon and metal-nitrogen lattice modes. Because the anion $[Al(NCN)_2]^-$ is isoelectronic with $Si(NCN)_2$, we postulate that $Li[Al(NCN)_2]$ may have a framework structure similar to that of $Si(NCN)_2$. This is essentially that of crystobalite SiO_2 in which the $–O^{-2}$ anion is replaced by the linear anion $(–N{=}C{=}N–)^{-2}$. The lithium counterions will probably occupy the interstitial tetrahedral sites thus formic the classic filled crystoballite structure. An excellent example of a filled crystoballite is $LiPN_2$ which is shown in Fig 3. Structure elucidation of $Li[Al(NCN)_2]$ is currently in progress.

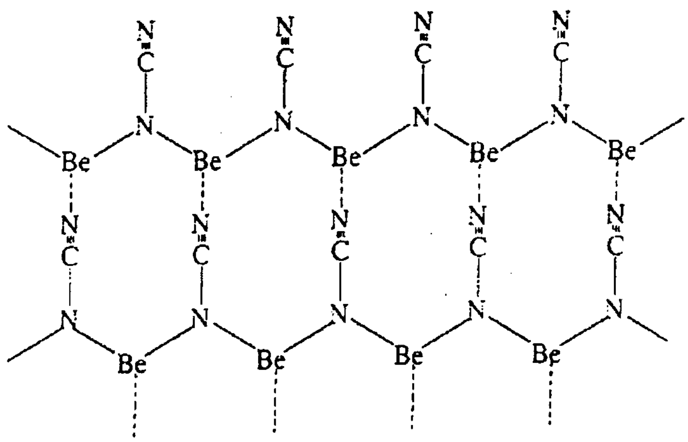
Figure 3: Structure of $LiPN_2$. The PN_2 array mimics that of isoelectronic SiO2 and the Li ions are sitting in interstitial tetrahedral sites.

C_3N_4 and $LiBC_4N_4$ under high pressure.

High pressure studies of C_3N_4 and diamond like $LiBC_4N_4$ were initiated with this project. Preliminary results results show that of the latter can be used to form pure and crystalline B-C-N with graphite like structure at 100 Kbar and 900°C (see D. Williams et al. J Am. Chem. Soc. 2000, 122, 7735) Experiments aimed to convert this compound into diamond-like dense structures are continuing in collaboration with Prof. Badding at Penn State University.

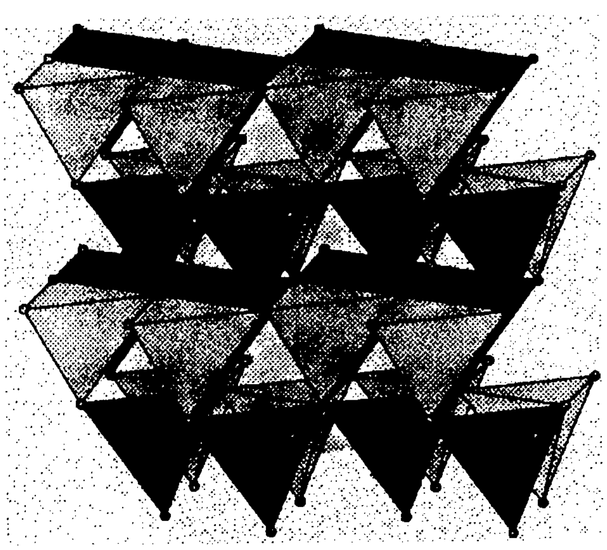
3. Personnel Supported

Cole Ritter
J. Kouvetakis
D. Walker



Possible polymeric structure of Be(N=C=N).

Figure 1. (top) Possible polymeric structure of Be(N=C=N). The structure of $BeSiN_2$ depicted as tetrahedra filled with Be (light) and Si (dark). (bottom) Tetrahedra filled with the same atoms form zig-zag chains. The three dimensional $BeCN_2$ compound is expected to have a similar dense structure.



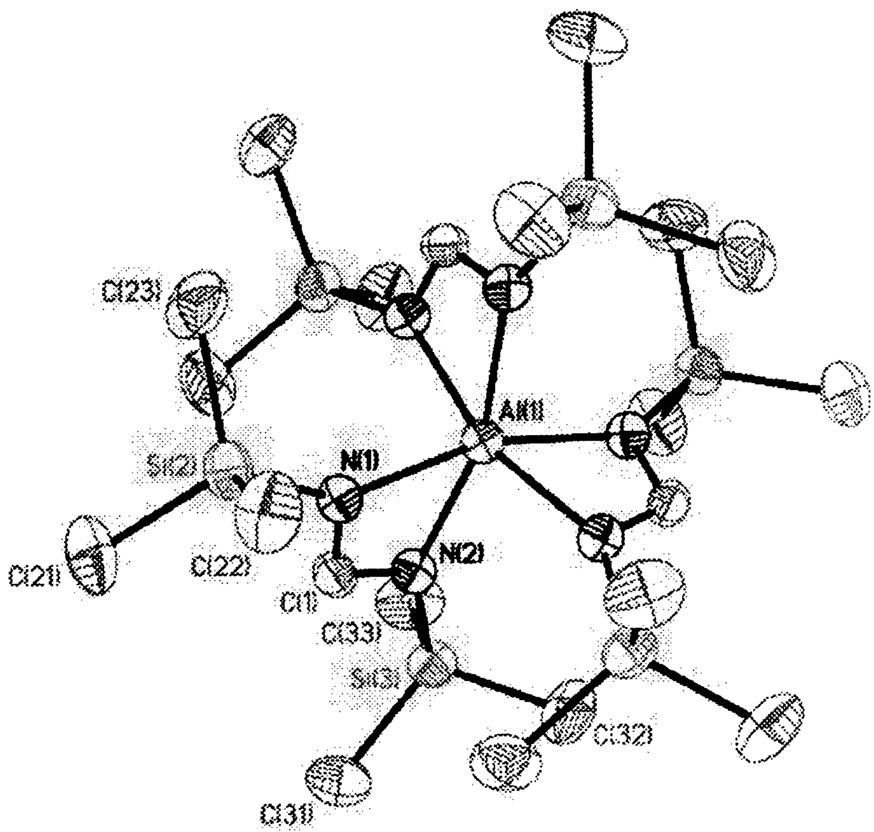


Figure 2. Molecular structure of $Al(Me_3Si{-}N{-}C{-}N{-}SiMe_3)_3$

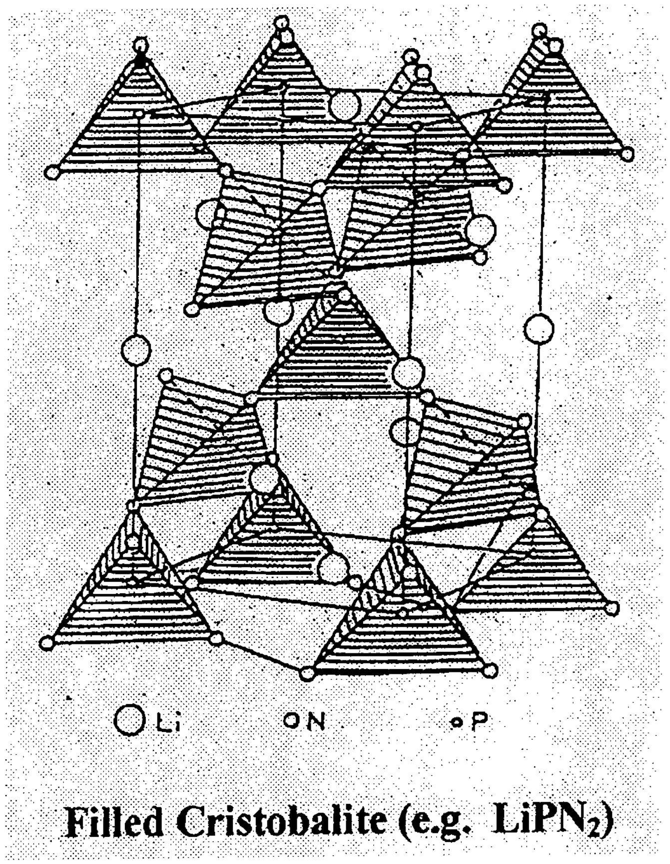


Figure 3. Structure of $LiPN_2$. The PN_2 array mimics that of isoelectronic SiO_2 and the Li ions are sitting in interstitial tetrahedral sites.